

Article

Thermodynamic Analysis of Alkali Metal Partitioning and Kaolin-Induced Phase Evolution During Wheat Straw Gasification

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Abstract

Alkali metal immobilization mediated by kaolin during wheat straw gasification was investigated using thermodynamic equilibrium calculations. Kaolin promoted the formation of stable K- and Na-bearing aluminosilicates, including feldspar, leucite, and nepheline. The controlling mechanism shifted from mineral-phase reactions below 1100 °C to a molten slag structure at higher temperatures. Increasing kaolin addition reduced the slag structure parameter R from 0.43 to 0.09, indicating enhanced network polymerization. The calculated evolution of Al-containing network units was consistent with enhanced K⁺/Na⁺ charge compensation around tetrahedrally coordinated Al, suggesting a possible structural origin for the increased thermodynamic stability of alkali metals. Gibbs free energy calculations demonstrated the improved thermodynamic stability of K and Na in the slag phase. At a kaolin addition of 5 wt.%, the K release fraction decreased by at least 29.36 percentage points relative to wheat-straw ash even at high temperatures over 1400–1600 °C. The results clarified the thermodynamic relationships among ash composition, phase evolution, and alkali partitioning during kaolin-assisted gasification.

Keywords: biomass gasification; alkali element release; mineral transformation; slag structure; Gibbs free energy

1. Introduction

The world is currently grappling with the dual challenges of the energy supply and environmental impact, particularly due to the excessive use of fossil fuels and the resulting greenhouse gas emissions [1,2]. The development of clean and renewable energy alternatives is therefore essential for addressing these challenges [3]. Biomass has been widely regarded as a promising option due to its renewable nature, zero-carbon emissions, and minimal nitrogen and sulfur content [4]. However, its large-scale utilization for energy production remains constrained by inherent characteristics, such as seasonal availability, low energy density, and low bulk density [5,6]. In contrast, coal remains one of the most abundant energy resources worldwide and benefits from a mature and well-established utilization infrastructure. Against this background, the co-gasification of biomass and coal has emerged as a promising conversion route [7,8]. It has offered several advantages, including lower carbon emissions, higher carbon conversion efficiency, and a broad range of applicable feedstocks. In addition, recent research underscored the potential benefits



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of the co-gasification of coal and biomass, which enhanced the gasification activity of coal char and reduced ash fusion temperatures [9].

Biomass feedstocks typically contain higher concentrations of alkali and alkaline earth metals (AAEMs) compared to coal, with potassium (K) and sodium (Na) being particularly prominent [10,11]. These elements can act as catalysts during gasification, improving the efficiency and reactivity of the process [12,13]. The catalytic action observed during gasification was primarily attributed to the alkali-based substances present at high temperatures, such as K_2O , Na_2O , and KCl [14]. An increase in the relative concentration of alkali metal oxides can further enhance this catalytic effect because alkali species can weaken or disrupt $C=O$ bonds and consequently reduce the activation energy of gasification reactions [15,16]. Research into the co-gasification of coal with various types of biomass, including woody biomass, agricultural residues, and municipal solid wastes, has demonstrated these effects [17]. For instance, it was found that the gasification rate improved when biomass additives constituted more than 20 wt.% [18]. Higher K contents in ash were also associated with greater gasification reactivity, and this catalytic enhancement became particularly evident when K-rich biomass was used as the co-gasification feedstock [19–21]. These studies collectively showed that the presence of alkali metals in biomass ash significantly promote gasification processes.

However, the beneficial catalytic effects of alkali metals are accompanied by their high volatility during gasification [22]. Potassium and sodium are known to be released into the gas phase during biomass gasification, leading to issues such as fouling, slagging, and sintering in gasification systems [23]. It has been reported that the temperature is an important factor influencing the release behavior of alkali metal elements [24]. Ash-related problems could arise even at temperatures as low as 850–900 °C because potassium (K) and sodium (Na) may partially volatilize and form minerals with low melting points [25]. During the devolatilization stage, potassium is primarily released as KCl , while in the char-reaction stage, it primarily exists as KOH [26]. The release of potassium could be divided into an initial-step release stage (<400 °C), the K-holding stage (400–700 °C), and the second-step release stage (>700 °C) [27]. At 1100 °C, potassium release can range from approximately 25% to 90%, depending strongly on the biomass properties and gasification conditions. By comparison, Na release is generally less sensitive to the temperature and becomes pronounced mainly above 1200 °C [28,29]. This is particularly concerning since the allowable concentration of alkali metals in fuel gas for combustion turbines in Integrated Gasification Combined Cycle (IGCC) systems is limited to 50 ppb [30]. Therefore, clarifying alkali-metal migration, release, and retention during biomass gasification is essential for controlling ash-related problems and improving the long-term stability.

To mitigate the negative impacts of alkali metals on the long-term operation of gasifiers and energy production, various strategies focusing on mineral reactions have been explored. High-silicon additives such as kaolin, high-silicon coal ash, and rice husk have been used to stabilize potassium and sodium by incorporating them into solid glassy slags [31]. Previous studies have examined the migration of alkali metals among volatile species, crystalline minerals, and ash/slag phases, with particular attention to potassium. Kaolin and mica additives were reported to substantially suppress K release during biomass combustion, with inhibition efficiencies of up to 90% for mica [32]. Aluminosilicate additives also significantly decrease K release during woody-biomass combustion [33]. Above 850 °C, alkali behavior becomes increasingly dependent on reactions among ash-forming minerals. K and Na can react with SiO_2 and Al_2O_3 to form silicates and aluminosilicates, including feldspar, nepheline, and melilite, thereby changing both alkali retention and the ash-melting behavior [34]. More recently, He et al. [35] used thermodynamic modeling to investigate kaolin-assisted alkali retention during corn-straw gasification. Their study

mainly explained why kaolin retained alkali metals under different temperature regimes, with an emphasis on alkali-bearing mineral evolution at relatively low temperatures and on the silicate-slag structure, Al-related charge compensation, and thermodynamic stability at elevated temperatures. However, the continuous relationship between additive-induced changes in the overall ash composition, the resulting migration across mineral-stability fields, and the element-specific redistribution of K and Na among gaseous, crystalline, and molten phases remained less explicitly addressed.

Despite these advances, the coupling among the bulk ash composition, phase stability, and alkali partitioning during progressive ash melting remains insufficiently understood. In particular, it is still unclear how the continuous compositional change induced by kaolin addition alters the preferred mineral fields and subsequently governs the distinct redistribution of K and Na as the ash evolves from a partially molten multiphase system to a fully molten slag. Most existing studies have focused either on individual mineral reactions at relatively low temperatures or on the properties of fully molten slags, while the continuous transition between these regimes has received comparatively less attention [36,37]. To address this issue, the present study established a composition–phase–partitioning framework for wheat-straw gasification using FactSage thermodynamic equilibrium calculations. The compositional trajectory of the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--K}_2\text{O--Na}_2\text{O--CaO}$ system was first analyzed to determine how progressive kaolin addition changed the dominant mineral-stability regions. Temperature-resolved elemental balances were then used to evaluate the redistribution of K and Na among gaseous species, crystalline phases, and liquid slag. Quenched-ash XRD measurements were employed to constrain the major predicted phase-transition tendency. At higher temperatures, slag structural parameters and Gibbs free-energy changes were further used to provide a thermodynamic interpretation of alkali retention in the molten phase. Through this integrated analysis, the study aimed to clarify the composition-dependent phase evolution and the differential partitioning behavior of K and Na, providing a theoretical basis for the rational selection of mineral additives and the mitigation of alkali-related problems during biomass gasification.

2. Experimental

2.1. Raw Materials

The wheat straw produced from Henan Province (China) was pulverized to less than 0.18 mm and then dried in an oven at 105 °C for 12 h for further analysis. The ultimate analysis of wheat straw was conducted using a Vario EL CUBE (Elementar Analysensysteme GmbH, Langenselbold, Germany), and the proximate analysis was performed using a 5E-MAG6600B industrial analyzer (Kaiyuan Instruments Co. Ltd., Hunan, China) based on GB/T 212-2008 (Chinese national standard) [38]. The proximate and ultimate analysis of wheat straw is shown in Table 1. Ion Chromatography (940 Professional IC Vario, Metrohm, Switzerland) was used to analyze the chlorine content of wheat straw, and the chlorine content of wheat straw is 4.23 wt.%.

Table 1. The proximate and ultimate analysis of wheat straw.

Proximate Analysis (wt.%, ad)					Ultimate Analysis (wt.%, daf)			
M	A	V	FC	C	H	N	S	O *
5.82	7.58	69.11	17.49	39.01	5.73	0.78	0.21	54.27

Abbreviations: ad, air dried basis; daf, dry and ash-free basis; *, by difference.

The kaolin was used as an additive to inhibit the release of alkali elements during straw gasification. The chemical composition of kaolin (produced from J&K Scientific

Company, Beijing, China) was analyzed via the X-ray fluorescence (XRF) based on GB/T 1574-2007 (Chinese national standard) and shown in Table 2. The added contents of kaolin were selected as 1 g, 2 g, 3 g, 4 g, and 5 g on the basis of 100 g wheat straw, and the blended samples were noted as WS-1K, WS-2K, WS-3K, WS-4K, and WS-5K, respectively.

Table 2. The chemical composition of wheat straw ash and kaolin.

Sample	Oxides, wt. %						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
WSA	54.36	2.86	1.85	4.92	2.99	2.43	24.86
Kaolin	57.22	39.98	0.98	0.33	0.49	0.11	0.89

2.2. Preparation of Wheat Straw Ash (WSA) and Its Analysis

The WSA was used to analyze the inorganic element content of wheat straw. To avoid the release of alkali elements, the WSA was prepared at 550 °C according to GB/T 28371-2012 (Chinese national standard) [39]. The chemical composition of WSA was analyzed via XRF and is listed in Table 2.

2.3. Quenched Slag Preparation and XRD Analysis

To ensure that the slag minerals kept a consistent structure with that at high temperatures, the sample was pulled out rapidly at target temperatures and quenched in ice water immediately. The mineral phases were analyzed using an X-ray powder diffract meter (BRUKER D8, Bruker AXS GmbH, Karlsruhe, Germany), with Cu K α radiation (40 kV, 100 mA). The progress was scanned with a step size of 0.02° over a 2 θ range of 10–90° [40].

2.4. Thermodynamic Modeling

The thermodynamic modeling software FactSage (version 7.3) enabled the calculation of phase equilibrium under the constrained condition. Further, the information regarding the phase structure, element distribution, and phase structure was also achieved. In this study, the thermodynamic calculation was used to simulate the gasification of wheat straw samples at different temperatures, with a particular focus on the transformation behavior of ash-forming elements. The “Equilib” and “Phase Diagram” module, together with the database “FToxid” and “FactPS”, were used to obtain the dominant phase distribution, phase composition, alkali element distribution, and bond structure. The temperature started at 800 °C and ended at 1600 °C at an interval of 50 °C.

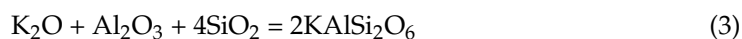
The FactSage calculations employed in this work represented equilibrium states obtained via Gibbs-energy minimization and should be interpreted as thermodynamic tendencies rather than a complete description of the transient gasification process. Actual alkali release can additionally be controlled by the heating rate, residence time, diffusion and mass transfer, volatilization kinetics, mineral crystallization/melting kinetics, and the formation of metastable phases. These kinetic effects were not resolved by the present equilibrium model. The quenched-ash XRD measurements provided experimental support for the major phase-transition sequence but did not directly determine the structure of the molten slag or the coordination state of Al. Consequently, the calculated bond distributions and charge-compensation relationships were used here to rationalize the equilibrium trends and provide theoretical guidance for practical gasification processes.

3. Results and Discussion

3.1. Alkali Element Release Properties of Wheat Straw

3.1.1. Dominant Phase-Area Distribution of Different Feedstocks

Based on the chemical composition of wheat straw ash and the addition of varying amounts of kaolin, a mineralogical phase diagram under the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--K}_2\text{O--Na}_2\text{O--CaO}$ system was constructed. In this diagram, SiO_2 , Al_2O_3 , and $\text{K}_2\text{O} + \text{Na}_2\text{O}$ were treated as variables, while the CaO content and the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio were kept constant. As shown in Figure 1, the black boundaries separated the primary mineral stability fields, while the colored contour lines represented the corresponding liquidus temperatures. The points WSA and WS-1K to WS-5K represented the continuous shift in the bulk ash composition caused by increasing kaolin addition. The original wheat-straw ash (WSA) was located in the Si-rich, Ca-silicate-dominated region, where CaSiO_3 was the main mineral. This can be represented schematically using Equation (1). As kaolin contained abundant SiO_2 and Al_2O_3 , progressive kaolin addition substantially increased the Al content of the ash. Consequently, the bulk composition moved away from the Ca-silicate stability region toward the K-bearing aluminosilicate fields. Under relatively Si-rich conditions, the increased availability of Al favored the incorporation of K into the feldspar-type structure KAlSi_3O_8 (Equation (2)). With further kaolin addition, the Al content continued to increase. Under these more Al-rich conditions, the formation of leucite became increasingly favorable (Equation (3)). Therefore, the trajectory from WSA to WS-5K represented more than a simple increase in the kaolin dosage. It reflected a progressive change in ash chemistry from a relatively Si-rich/Ca-silicate system toward an Al-enriched alkali–aluminosilicate system. This compositional shift changed the thermodynamically preferred host phases of potassium from Ca-associated silicate surroundings toward KAlSi_3O_8 and subsequently KAlSi_2O_6 -type structures. This result indicated that kaolin can effectively stabilize the alkali metals in WSA. This indicated that kaolin, as an additive, effectively stabilized the alkali metals in WSA. This effect was attributed to the increased content of SiO_2 and Al_2O_3 , which led to the formation of aluminosilicate phases during the melting process [41]. The increasing aluminosilicate prevented the volatilization of alkali metals into the gas phase. Although the phase diagrams could provide general trend information, the specific transformation and solidification mechanisms still need to be further analyzed.



3.1.2. Alkali Element Migration Properties During Wheat Straw Gasification

The migration characteristics of alkali metals (K and Na) during wheat straw gasification are illustrated in Figure 2. From Figure 2a, the proportion of alkali metal release increased with a rising temperature. Within the temperature range of 800–1100 °C, the increase was relatively modest. However, as the temperature continued to rise, the release rate gradually accelerated. It was particularly pronounced in the release of sodium (Na). Additionally, the release proportion of potassium (K) (40–75% wt.%) was higher than that of sodium (15–45% wt.%). To further analyze the migration and transformation behavior of alkali metals in the ash, thermodynamic calculations of high-temperature slag compositions were performed. According to Figure 2b, at 800 °C, the phases presented in WSA included the liquid phase, feldspar ((K,Na)AlSi₃O₈), clinopyroxene ((Ca,Mg)Si₂O₆), and potassium chloride (KCl). As the temperature increased, alkali-metal-bearing phases such as feldspar

and KCl completely melted at 950 °C. With a further increase in temperature, clinopyroxene changed to a liquid phase, eventually melting completely at 1276 °C.

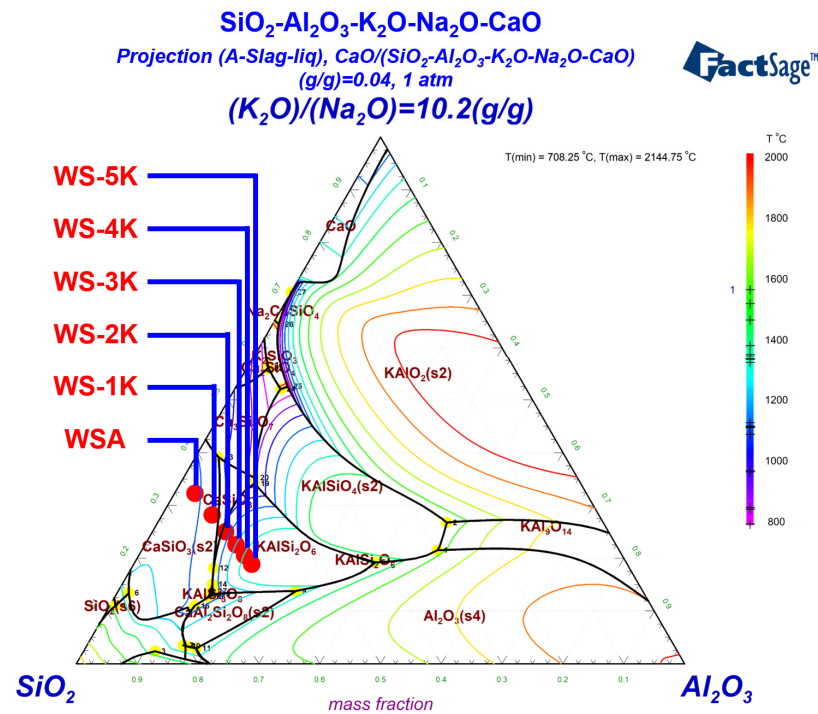


Figure 1. Phase diagram under the SiO₂-Al₂O₃-K₂O-Na₂O-CaO system.

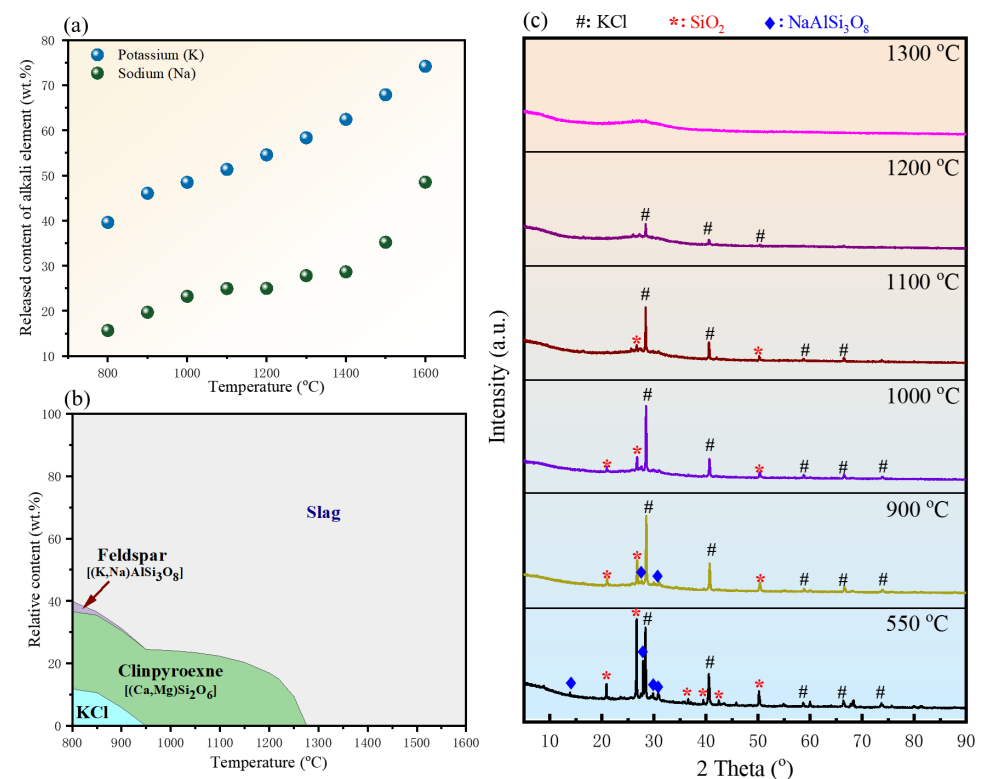


Figure 2. Alkali metal element release and transformation behavior of wheat straw during the gasification condition. (a) The distribution of K and Na in the gaseous phase; (b) K- and Na-bearing mineral evolution in the slag phase with various temperatures; (c) XRD patterns of wheat straw ashes at different quenching temperatures.

Comparing the thermodynamic calculation results with the phase changes observed under real conditions (Figure 2c), there were some discrepancies in the crystalline phases. The initial mineral phases in WSA include KCl, SiO₂, and feldspar. As the temperature rose, the feldspar disappeared first, and the intensities of KCl and SiO₂ also gradually decreased. At 1300 °C, all mineral phases were converted to a liquid amorphous glassy slag, which was consistent with the thermodynamic calculation results. The agreement between the thermodynamic calculation and XRD observations is more appropriately evaluated in terms of the major phase-transition windows and overall evolution trends. FactSage predicts the disappearance of feldspar at approximately 950 °C, which is consistent with its experimentally observed disappearance between 900 and 1000 °C. Likewise, the predicted transition toward a fully molten state at approximately 1276 °C agrees reasonably well with the gradual weakening of crystalline diffraction peaks and the formation of an essentially amorphous slag at 1300 °C. Some deviations remain for individual phases; for example, KCl persists experimentally to temperatures higher than its equilibrium disappearance temperature, which may be associated with kinetic limitations, mass-transfer effects, volatilization behavior, metastable phase persistence, and possible structural changes during heating and quenching. Therefore, although the experimental system cannot exactly reproduce the thermodynamic equilibrium state, the overall phase-evolution tendency is consistent with the calculation. Moreover, the release behavior of alkali metals was determined by gas, liquid, and solid phases in the real condition [42]. The thermodynamic simulation results were related to phases at an equilibrium state and were independent of the reaction process, particularly the mass transfer [43]. Accordingly, the present work mainly uses FactSage to analyze the thermodynamic feasibility, phase-transition tendency, and equilibrium alkali-partitioning behavior rather than to quantitatively reproduce the actual transient gasification process. In future work, we will further strengthen this validation through controlled gasification experiments, quantitative phase analysis, and direct measurements of gaseous and condensed alkali species.

3.2. Effect of Kaolin Proportion on the Mineral Transformation Property

Figure 3 illustrates the evolution of mineral phases in the ash with varying proportions of kaolin addition. For WS-1K (Figure 3a), the primary mineral phases were similar to those in wheat straw ash, mainly consisting of feldspar, clinopyroxene, and KCl. However, the content of KCl was significantly reduced, while the amounts of feldspar and clinopyroxene increased. As the proportion of kaolin was increased (Figure 3b), in sample WS-2K, the KCl phase disappeared, and a new phase (leucite (KAlSi₂O₆)) emerged. This change was primarily due to the increased amounts of SiO₂ and Al₂O₃, which tended to form more stable alkali-based mineral phases. When the kaolin addition reached 3 wt.% (Figure 3c, WS-3K), there was no liquid phase at low temperatures. Moreover, the contents of alkali-metal-bearing minerals, such as feldspar and leucite, also increased significantly. Additionally, a substantial amount of SiO₂ and Al₂O₃ reacted with elements like magnesium and iron to form a new phase, olivine ((Mg,Fe)₂SiO₄). In Figure 3d, WS-4K exhibited the same mineral phases as WS-3K, but with an increasing proportion of leucite as the kaolin content increased. This indicated that a higher proportion of alkali metals was fixed in the slag. This trend was even more pronounced in WS-5K (Figure 3e), where the proportions of feldspar and leucite approached 85 wt.%. Additionally, a small amount of nepheline (NaAlSi₃O₈) was formed, which had a sodium-fixation effect. The release of alkali metals was primarily determined by the composition of mineral phases and the characteristics of the liquid slag [44]. The results indicated that the chemical reactions between ash components at low temperatures were the major factor influencing alkali release behavior. As the proportion of the kaolin content increased, the variety and proportion of alkali-bearing mineral phases

were enhanced. Hence, the addition of kaolin as an additive was an effective method for stabilizing alkali metals in biomass and reducing sintering hazards during gasification.

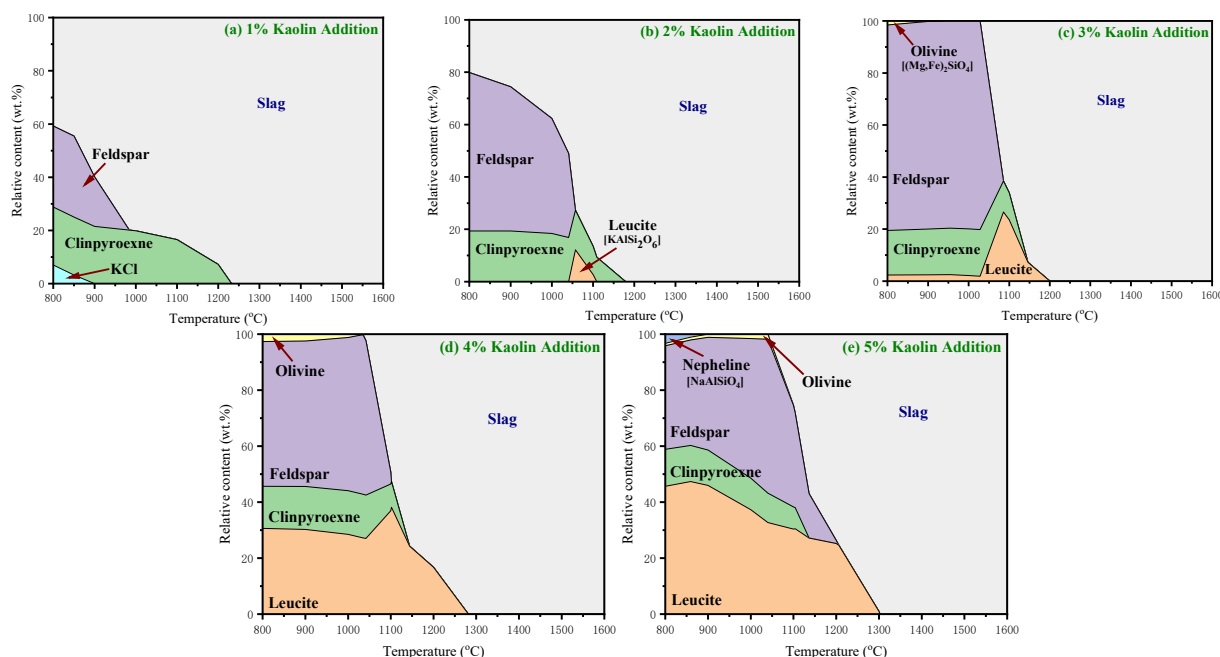


Figure 3. The mineral phase evolution under different kaolin addition ratios. Feldspar: $(K,Na)AlSi_3O_8$. Clinpyroxene: $(Ca,Mg)Si_2O_6$. Leucite: $KAlSi_2O_6$. Olivine: $(Mg,Fe)_2SiO_4$. Nepheline: $NaAlSiO_4$.

3.3. Effect of Kaolin Addition on K and Na Release Behavior

Based on the clarified evolution of mineral phases, the migration and release characteristics of alkali metals at different kaolin addition ratios and temperatures were analyzed. The results, characterized by the content of alkali metals migrating to the gas phase, are shown in Figure 4. For potassium (K) release (Figure 4a), the proportion in the gas phase increased with the rising temperature. At the same temperature, the K release proportion decreased as the kaolin content increased, indicating that kaolin addition significantly inhibited K release. Regarding sodium (Na) release (Figure 4b), the trend was first increased and then decreased with increasing kaolin addition. Additionally, the kaolin content corresponding to the maximum release point changed with the temperature. This behavior was divided into three stages: Stage I (800–1100 °C), where the maximum release occurred with 3 wt.% kaolin addition; Stage II (1200–1400 °C), where the maximum release was observed with 2 wt.% kaolin addition; and Stage III (1500–1600 °C), where the maximum release point shifted to 1 wt.% kaolin addition. The differences in K and Na release characteristics were related to their respective ash chemistry, mineral phase, and liquid phase contents [45]. In addition, the qualitative transition from mineral-phase-controlled alkali retention at relatively low temperatures to slag-structure-controlled retention after complete melting agrees with the mechanism reported by He et al. [35] for corn straw. The result indicated that this general framework can be extended to wheat-straw ash. However, the detailed alkali partitioning is feedstock dependent. This differs from the behavior reported for corn straw and reflects differences in the evolution of the liquid-slag fraction and Na-bearing feldspar/nepheline phases. Overall, higher kaolin addition significantly enhanced the stabilization of K and Na. Particularly for K, at 1400–1600 °C, increasing the kaolin dosage to 5 wt.% decreased the calculated K release fraction by at least 29.36 percentage points compared with that of WSA without kaolin addition. This demonstrated that the inhibitory effect remained pronounced even after the ash became predominantly molten.

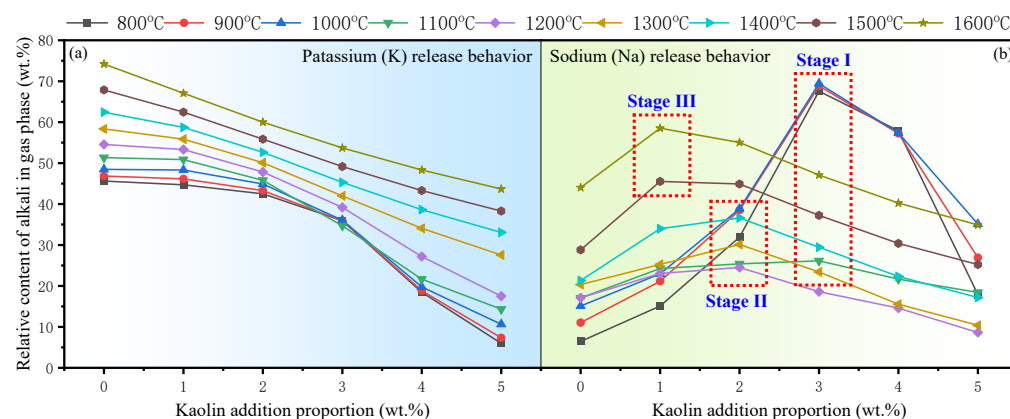


Figure 4. Potassium (K, (a)) and sodium (Na, (b)) releasing behavior at different kaolin addition ratios and different temperatures.

3.3.1. Elemental Balance Analysis of Potassium of Different Feedstocks

To further quantitatively analyze the migration characteristics of alkali metals in the solid and liquid phases, elemental balances for K and Na were performed. The migration characteristics of K are illustrated in Figure 5. For all samples, the content of K in the solid phase gradually decreased with the increasing temperature. However, with the increase in kaolin content, there were notable changes in the mineral phase composition. For raw wheat straw, the potassium-bearing solid phase was solely KCl. Its content decreased from 29.53 wt.% at 800 °C to 13.81 wt.% at 900 °C, leading to an increase in the K content in the gas phase. As the kaolin content increased, the content of potassium-bearing phases increased. Comparing WS-1K and WS-2K, KAlSi_3O_8 was a newly formed potassium mineral. At 800 °C, its content increased from 34.60 wt.% in WS-1K to 73.92 wt.% in WS-2K. When the kaolin content exceeded 3 wt.%, KAlSi_2O_6 began to precipitate, and its proportion increased with kaolin addition. At 800 °C, the contents of KAlSi_2O_6 in WS-3K, WS-4K, and WS-5K were 3.82 wt.%, 44.97 wt.%, and 64.96 wt.%, respectively. WS-5K also contained a small amount of KAlSiO_4 . These results indicated that as the kaolin content increased, the reaction of potassium with SiO_2 and Al_2O_3 to form KAlSi_3O_8 and KAlSi_2O_6 was the main reason for the inhibition of potassium release.

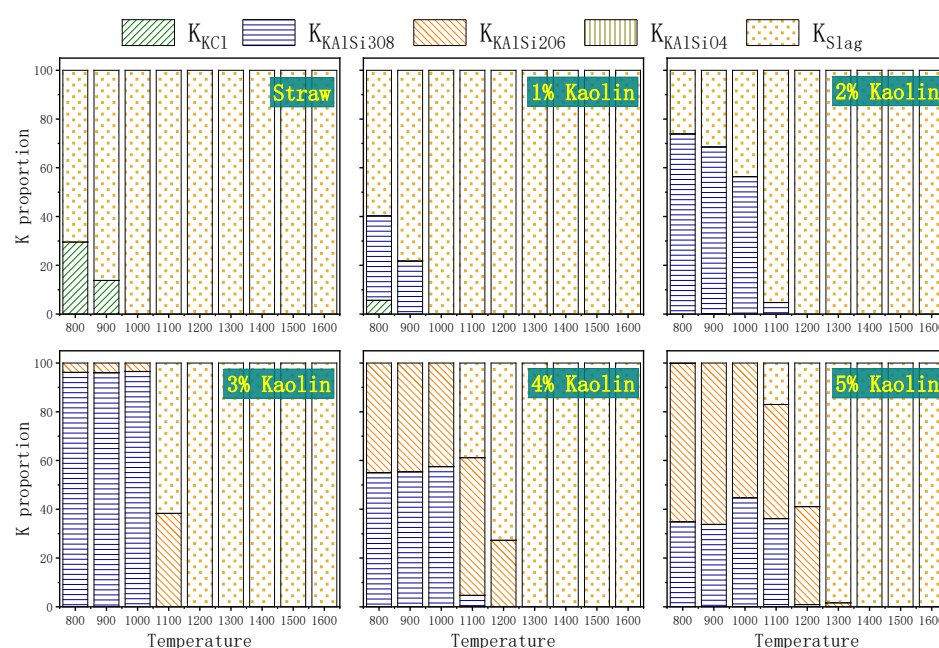


Figure 5. Potassium elemental balance calculation and distribution in the slag phase.

3.3.2. Elemental Balance Analysis of Sodium of Different Feedstocks

The migration characteristics of sodium are shown in Figure 6. The types of sodium-bearing minerals in the solid phase were limited, primarily including $\text{NaAlSi}_3\text{O}_8$ and NaAlSiO_4 . There were no sodium-bearing solids presented in the WSA, indicating that the liquid slag played a critical role in fixing Na. As the kaolin content increased, $\text{NaAlSi}_3\text{O}_8$ first formed, with its content increasing from 9.71 wt.% in WS-1K to 100 wt.% in WS-3K, representing another important factor influencing Na release. In WS-5K, nepheline (NaAlSiO_4) appeared with a content of 36.13 wt.% and melted into the liquid phase at 1100 °C. Analyzing the release characteristics of Na in the gas phase, at lower temperatures (800–1100 °C, Stage I), a substantial amount of Na was present in the liquid phase. The addition of kaolin caused a rapid decrease in the liquid phase, leading to an increase in the Na release proportion. At a kaolin addition of 3 wt.%, the liquid phase was nearly eliminated, resulting in the highest release rate. However, the significant formation of feldspar at 1100 °C mitigated this effect, and the Na release rate decreased significantly. With a further temperature increase (1200–1400 °C, Stage II), Na release was controlled by both mineral phases and the liquid phase. As the kaolin content increased, Na first converted to the solid phase and then melted into the liquid phase. The increased SiO_2 and Al_2O_3 contributed to the stabilization of Na_2O , causing the maximum release point to shift to lower kaolin addition [46]. At high temperatures (1500–1600 °C, Stage III), the liquid phase was 100 wt.%, and Na release was primarily controlled by the liquid phase. With high kaolin addition, a significant amount of Na was first fixed due to the formation of feldspar and nepheline, leading to the low sodium release.

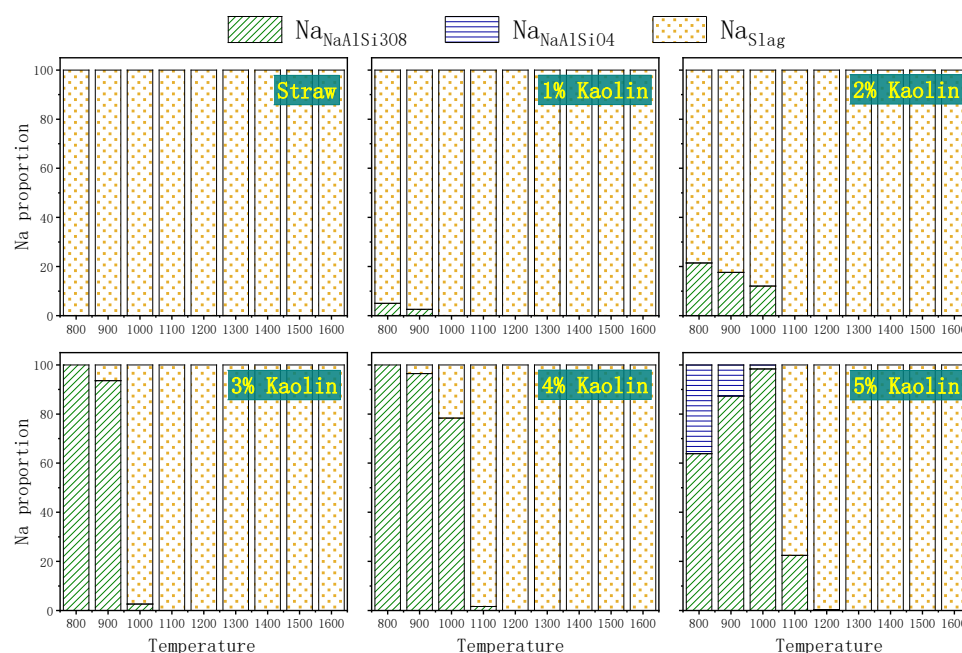


Figure 6. Sodium elemental balance calculation and distribution in the slag phase.

3.4. Alkali Release Mechanism in the Liquidus Molten Slag

When the gasification temperature exceeded the temperature at which the slag became fully liquid, the ash slag consisted of a silicate melt [47]. At this stage, the structure of the slag was closely related to the release behavior of alkali metals [48]. The slag structure can be described by using a three-dimensional network model. The tetrahedrally coordinated Si^{4+} or Al^{3+} (IV) ions were linked by bridging oxygens (BO) to form a network structure, increasing the slag polymerization degree [49]. Alkaline components such as Ca^{2+} , Mg^{2+} , K^+ , and Na^+ disrupted the tetrahedra structure, converting bridging oxygens to non-

bridging oxygens (NBOs), reducing the slag polymerization degree [50]. The degree of network polymerization was quantitatively described using the slag structure parameter R (the ratio of non-bridging oxygens to bridging oxygens, NBO/BO). A larger R value indicated a lower degree of network polymerization [51]. The R value could be calculated using Equation (4), where the components were expressed in molar fractions.

$$R = \frac{\text{NBO}}{\text{BO}} = \frac{\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3}{\text{SiO}_2 + 2 \times (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)} \quad (4)$$

The highest temperature at which the slag was fully molten was 1306 °C for WS-5K. To ensure that all analyzed samples were in a completely liquid state, temperatures above 1400 °C were selected for analysis. The impact of the slag structure on alkali metal release processes is shown in Figure 7. From Figure 7a, the value of the R value decreased with increasing kaolin addition, significantly dropping from 0.43 for WSA to 0.09 for WS-5K. This indicated that kaolin addition effectively enhanced the network polymerization of the liquid slag. The relationship between the R values and the release characteristics of alkali metals K and Na is shown in Figure 7b. The release proportion of potassium increased with an increasing R value. This suggested that a decrease in the slag polymerization degree facilitated potassium release. Si^{4+} and Al^{3+} in the slag contributed to network formation, aiding in the creation of silicate network structures [52]. Therefore, the addition of kaolin lowered the R value of the melt and reduced the K release proportion. Additionally, the R value of the melt reduced the proportion of released K. In contrast to K, the release rate of Na first increased and then decreased with the increasing R values. The maximum release rate occurred when R was between 0.2 and 0.3, which was related to the distribution of network-forming component chemical bonds in the silicate melts and the charge compensation effect of alkali metals [53].

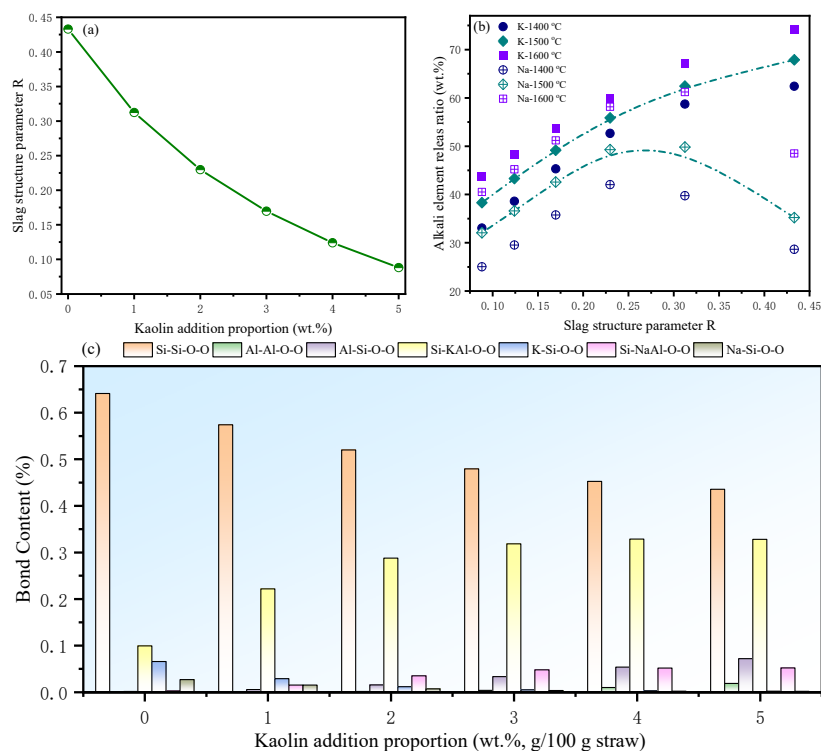
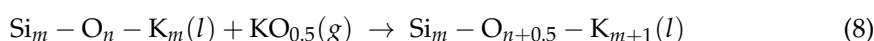
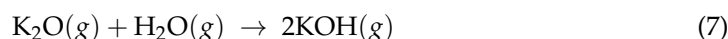
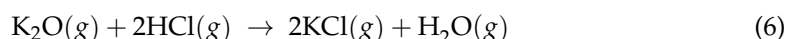
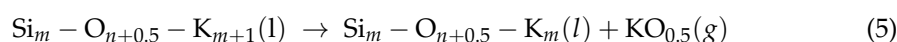


Figure 7. Effect of the slag structure on the release mechanism of the alkali element. (a) Effects of kaolin addition on the slag polymerization degree (slag structure parameter R); (b) the relationship between the R value and release behavior of alkali elements; (c) effect of kaolin addition on the Si-Al and alkali-bearing chemical bond structures in the molten slag at 1400–1600 °C.

Figure 7c shows that with increasing kaolin addition, the content of Si-Si-O-O structures in the slag decreased, while the content of Al-Al-O-O and Al-Si-O-O structures increased. This indicated that the increased slag polymerization degree was primarily due to the increased content of Al-Si-O-O structural units. Additionally, as kaolin addition increased, the content of Si-KAl-O-O structural units in the slag increased, while the content of K-Si-O-O structural units decreased. Moreover, the content of Si-NaAl-O-O structural units initially increased and then remained constant, while the content of Na-Si-O-O structural units decreased. Compared to Si^{4+} , the tetrahedrally coordinated Al^{3+} in the slag required alkali metal ions (Na^+ and K^+) for charge compensation. Therefore, the calculated fraction of Al-containing network units increased together with the predicted Si-KAl-O-O and Si-NaAl-O-O units along with the increasing kaolin addition. Because tetrahedrally coordinated Al^{3+} in aluminosilicate networks requires charge compensation by monovalent cations, this trend is consistent with the participation of K^+ and Na^+ as charge-compensating species [54]. The thermodynamic results suggested that increased incorporation of Al into the silicate network may enhance alkali retention through charge-compensation interactions [55]. However, the Al coordination state was not directly measured in the present study, and this interpretation should consequently be regarded as a model-supported mechanism rather than direct structural evidence.

3.5. Analysis of the Alkali Release Reaction in Slag Based on Gibbs Free Energy

The release characteristics of alkali metals from slag were related to the Gibbs free energy of the release process and could be used to investigate the solidification mechanism of alkali metal [56]. According to the thermodynamic calculation, the release of alkali metals in the slag consisted of two processes: the generation of intermediate products and their release. Taking K as an example, the intermediate product $\text{KO}_{0.5}(\text{g})$ (Equation (5)) was first generated during the high temperature. Then, the intermediate product was released by reacting with the gas-phase medium to form $\text{KCl}(\text{g})$ and $\text{KOH}(\text{g})$ (Equations (6) and (7)). Under melting conditions, the proportion of K and Na released was expressed as $f(\text{K})$ and $f(\text{Na})$, respectively. The chlorine and water vapor content in the gas phase under a high temperature were less affected by the kaolin addition. The main variable was the slag chemical composition. Hence, Equation (5) was used to describe the alkali metal release process and Equation (8) was used to represent the solidification reaction of alkali metal. The smaller the Gibbs free energy $\Delta G(\text{K})$ of the reaction, the easier the reaction occurred, i.e., the stronger the slag's ability to fix potassium alkali elements.



Equations (6) and (7) are the $\Delta G(\text{K})$ and equilibrium constant $K(\text{K})$ for Equation (5)

$$\Delta G(\text{K}) = -RT \ln K(\text{K}) \quad (9)$$

$$K(\text{K}) = (P(\text{KO}_{0.5})/P)^{-1} \quad (10)$$

where R is the gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; T is the temperature, K; $P(\text{KO}_{0.5})$ is the partial pressure of gaseous alkali metal, Pa; and P is the system pressure, Pa. Since the slag is in the condensed phase, only the partial pressure of the gaseous alkali metals contributes to the equilibrium constant. By combining Equations (9) and (10), we obtain Equation (11).

Then, the relation between $\ln f(K)$ and $1/T$ is linear (Equation (12)), with the slope equal to $\Delta G(K)/R$.

$$\ln \left(\frac{P(KO_{0.5})}{P} \right) = \Delta G(K)/(RT) \quad (11)$$

$$\ln f(K) \propto \Delta G(K)/(RT) \quad (12)$$

The alkali metal release ratios $f(K)$ and $f(Na)$ were determined based on the FactSage calculation for samples in the temperature range of 1400 °C to 1600 °C. By plotting $10,000/T$ on the X-axis and $\ln f(K)$ or $\ln f(Na)$ on the Y-axis, as shown in Figure 8a,b, a good linear relationship between $\ln f(K)$ or $\ln f(Na)$ and $1/T$ was obtained. The slope of this line provided the Gibbs free energy (ΔG) for the fixation of alkali metals in the slag. A smaller slope indicated that the process described by Equation (5) was more thermodynamically favorable, meaning that the slag had a stronger ability to fix alkali metals. From Figure 8c, with increasing kaolin addition, the ΔG for fixing potassium and sodium in the slag generally decreased, indicating an enhanced ability of the slag to fix alkali metals. Additionally, for slags with the same chemical composition, $\Delta G(K)$ was always higher than $\Delta G(Na)$. The result suggested that potassium was more readily released into the gas phase compared to sodium, which may be related to the lower ionic potential of K^+ .

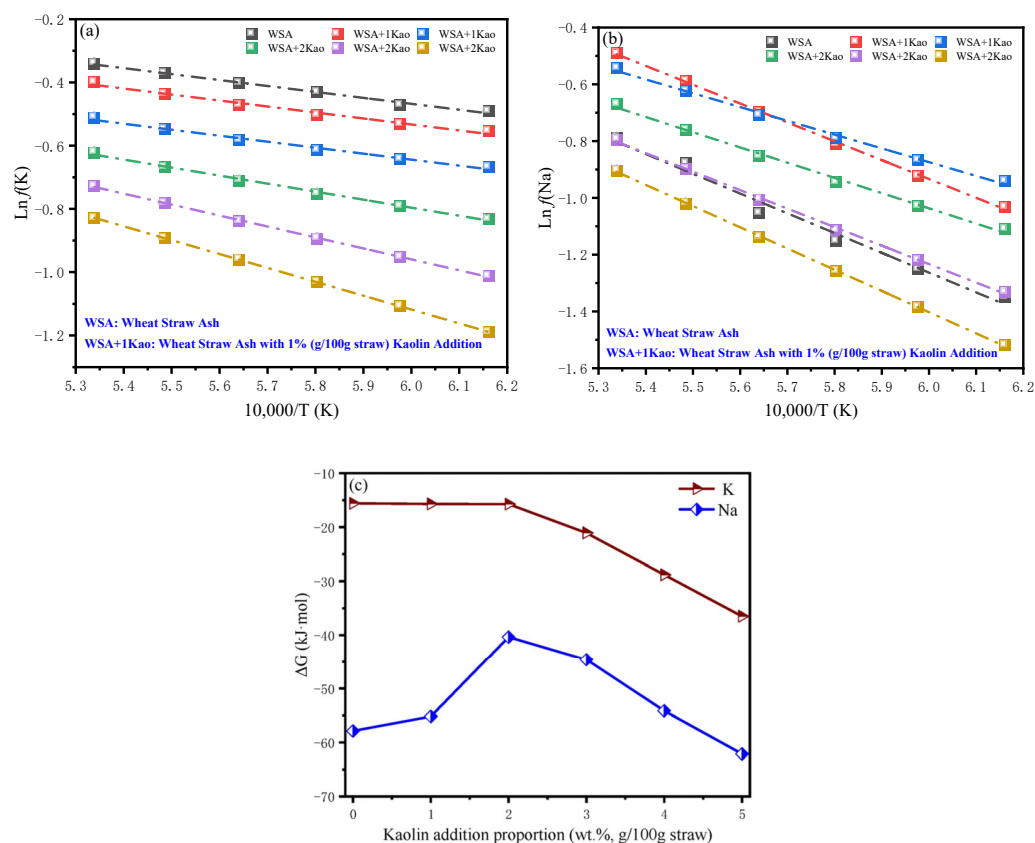


Figure 8. Effect of kaolin addition on the Gibbs free energy of the alkali element release reactions in slag. (a) Relationship between the released K content and temperature; (b) relationship between the released Na content and temperature; (c) the changes in $\Delta G(K)$ and $\Delta G(Na)$ with different ratios of kaolin addition.

The present study established a predictive model for alkali-metal migration and immobilization under thermodynamic equilibrium conditions, which was mainly used to characterize the thermodynamic trends of phase evolution and K/Na partitioning at different temperatures and kaolin addition levels. To further assess the reasonableness

of the predicted results, we compared them with experimental observations reported in the literature. Previous studies [29,57,58] showed that kaolin addition significantly increased K retention in ash and promoted the formation of stable K-Al-Si phases such as orthoclase, leucite, and kalsilite. Online gas-phase measurements also demonstrated that kaolin effectively reduced the release of KCl and overall gaseous alkali species. For Na, flame-emission spectroscopy, XRF, XRD, and SEM-EDS analyses likewise showed that kaolin decreased gaseous Na concentrations and promoted Na incorporation into stable aluminosilicate phases such as nepheline. These experimental observations were in good agreement with the overall thermodynamic trends predicted in the present study, namely that kaolin promoted the redistribution of K and Na into stable aluminosilicate phases and suppressed their transfer to the gas phase. It should be noted that differences in feedstocks, atmospheres, and reactor configurations among these studies mean that the literature results can only be used to support the reasonableness of the predicted trends rather than as a substitute for direct quantitative validation of the present system. A rigorous quantitative validation of the equilibrium predictions will still require experiments conducted under boundary conditions closely matching those used in the calculations, while the effects of kinetic and mass-transfer limitations should also be further clarified.

4. Conclusions

This study has elucidated the impact of kaolin addition on the release behavior of alkali metals (potassium and sodium) during the gasification of wheat straw through comprehensive thermodynamic modeling. The findings underscore that the presence of alkali metals predominantly in the forms of feldspar, leucite, and nepheline plays a pivotal role in influencing their release during gasification. The main conclusions can be drawn as follows:

(1) At lower temperatures, the chemical reactions between ash components primarily control alkali metal release during the gasification process. Kaolin could promote the formation of minerals with better alkali metal capture capabilities, such as feldspar ($(\text{K,Na})\text{AlSi}_3\text{O}_8$), leucite (KAlSi_2O_6), and nepheline (NaAlSiO_4).

(2) At higher temperatures, the slag structure is responsible for the release of alkali elements. The addition of kaolin decreases the R value of the slag, leading to the polymerization of slag and therefore inhibiting alkali element release. The calculated slag structural evolution is consistent with an increased contribution of Al-containing network units and associated charge-compensation interactions involving K^+ and Na^+ .

(3) The addition of kaolin increases the Gibbs free energy of the alkali element release reaction in the slag, suppressing the alkali element release. In addition, the ΔG of the slag fixing K is lower than that of Na. Consequently, the K is more prone to be released than Na in the slag of WSA.

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